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Liu et al.

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(54) **METHOD OF PASSIVATING CHEMICAL MECHANICAL POLISHING COMPOSITIONS FOR COPPER FILM PLANARIZATION PROCESSES**

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This patent is subject to a terminal disclaimer.

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(22) Filed: **Sep. 19, 2008**

(65) **Prior Publication Data**

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Related U.S. Application Data

(63) Continuation of application No. 11/117,282, filed on Apr. 28, 2005, now abandoned, and a continuation-in-part of application No. 10/315,641, filed on Dec. 10, 2002, now Pat. No. 7,300,601.

(51) **Int. Cl.**
H01L 21/302 (2006.01)
B44C 1/22 (2006.01)

(52) **U.S. Cl.** **438/693**; 438/691; 438/692; 216/88; 216/89

(58) **Field of Classification Search** 216/88, 216/89; 438/691, 692, 693
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,114,215	A *	9/2000	Osugi et al.	438/401
6,168,508	B1 *	1/2001	Nagahara et al.	451/527
6,184,141	B1	2/2001	Avanzino et al.	
6,190,237	B1	2/2001	Huynh et al.	
6,303,049	B1	10/2001	Lee et al.	
6,312,486	B1	11/2001	Sandhu et al.	
6,383,414	B1 *	5/2002	Pasch	252/389.21
6,428,721	B1	8/2002	Ina et al.	

(Continued)

FOREIGN PATENT DOCUMENTS

EP 1081200 A1 3/2001

(Continued)

OTHER PUBLICATIONS

Patent Cooperation Treaty, International Preliminary Report on Patentability, Nov. 13, 2009.

(Continued)

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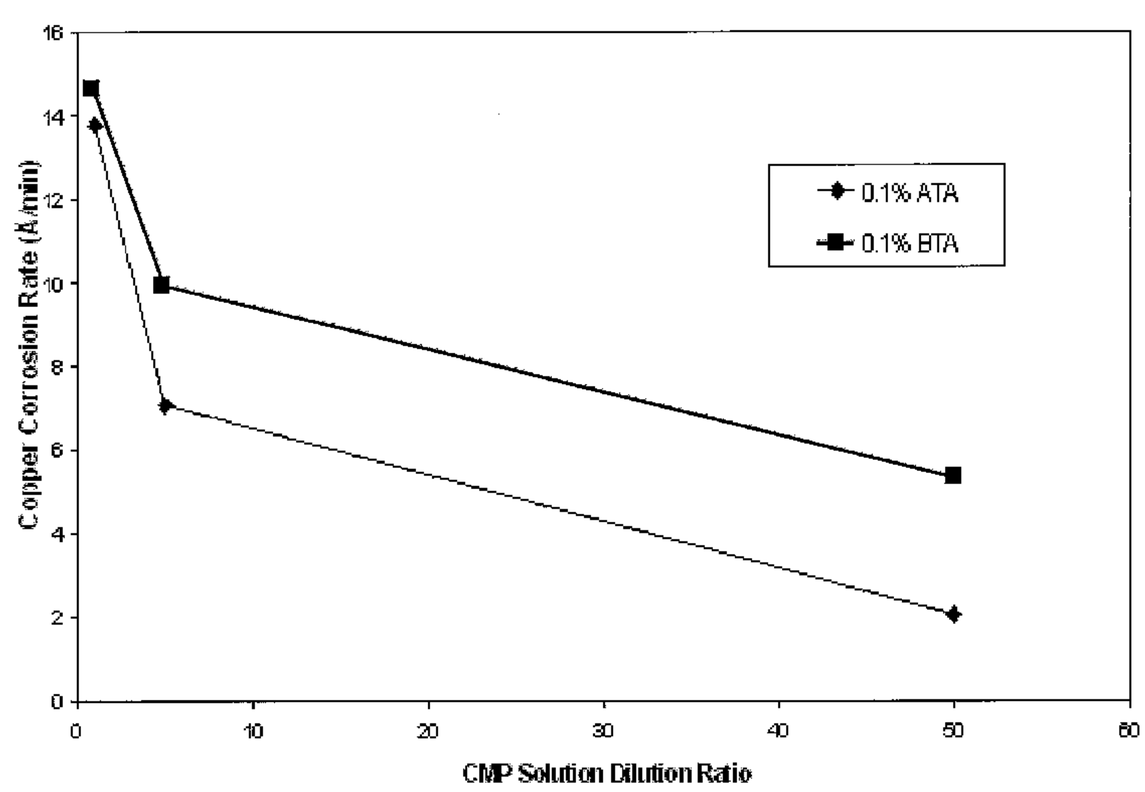
(74) *Attorney, Agent, or Firm* — Tristan A. Fuierer; Moore & Van Allen, PLLC; Rosa Yaghmour

(57) **ABSTRACT**

A method of passivating a CMP composition by dilution and determining the relationship between the extent of dilution and the static etch rate of copper. Such relationship may be used to control the CMP composition during the CMP polish to minimize the occurrence of dishing or other adverse planarization deficiencies in the polished copper, even in the presence of substantial levels of copper ions in the CMP composition and at the copper/CMP composition interface.

20 Claims, 6 Drawing Sheets



U.S. PATENT DOCUMENTS

6,429,134	B1	8/2002	Kubota et al.	
6,440,186	B1	8/2002	Sakai et al.	
6,447,695	B1	9/2002	Motonari et al.	
6,569,350	B2	5/2003	Kaufman et al.	
6,593,239	B2	7/2003	Kaufman et al.	
6,638,854	B2	10/2003	Homma et al.	
6,656,842	B2	12/2003	Li et al.	
6,805,812	B2	10/2004	Fang	
6,811,470	B2	11/2004	Bonner et al.	
6,867,138	B2 *	3/2005	Miyashita et al.	438/691
6,910,954	B2	6/2005	Kim et al.	
6,936,543	B2	8/2005	Schroeder et al.	
7,132,058	B2	11/2006	Thomas et al.	
2001/0008828	A1	7/2001	Uchikura et al.	
2002/0005017	A1	1/2002	Motonari et al.	
2002/0111024	A1	8/2002	Small et al.	
2003/0036339	A1	2/2003	Bonner et al.	
2004/0025444	A1	2/2004	Small et al.	

FOREIGN PATENT DOCUMENTS

EP	1138733	A2	10/2001
EP	1138734	A2	10/2001
EP	1628334	A1	2/2006
TW	499471	B	8/2002

OTHER PUBLICATIONS

Supplementary European Search Report for EP 0381 2786 dated Nov. 30, 2005.

Aksu, S., et al., J. Electrochem. Soc., 149(6), G352-G361 (2002).

Hariharaputhiran, M. et al., J. Electrochem. Soc., 147(10), 3820-3826 (2000).

* cited by examiner

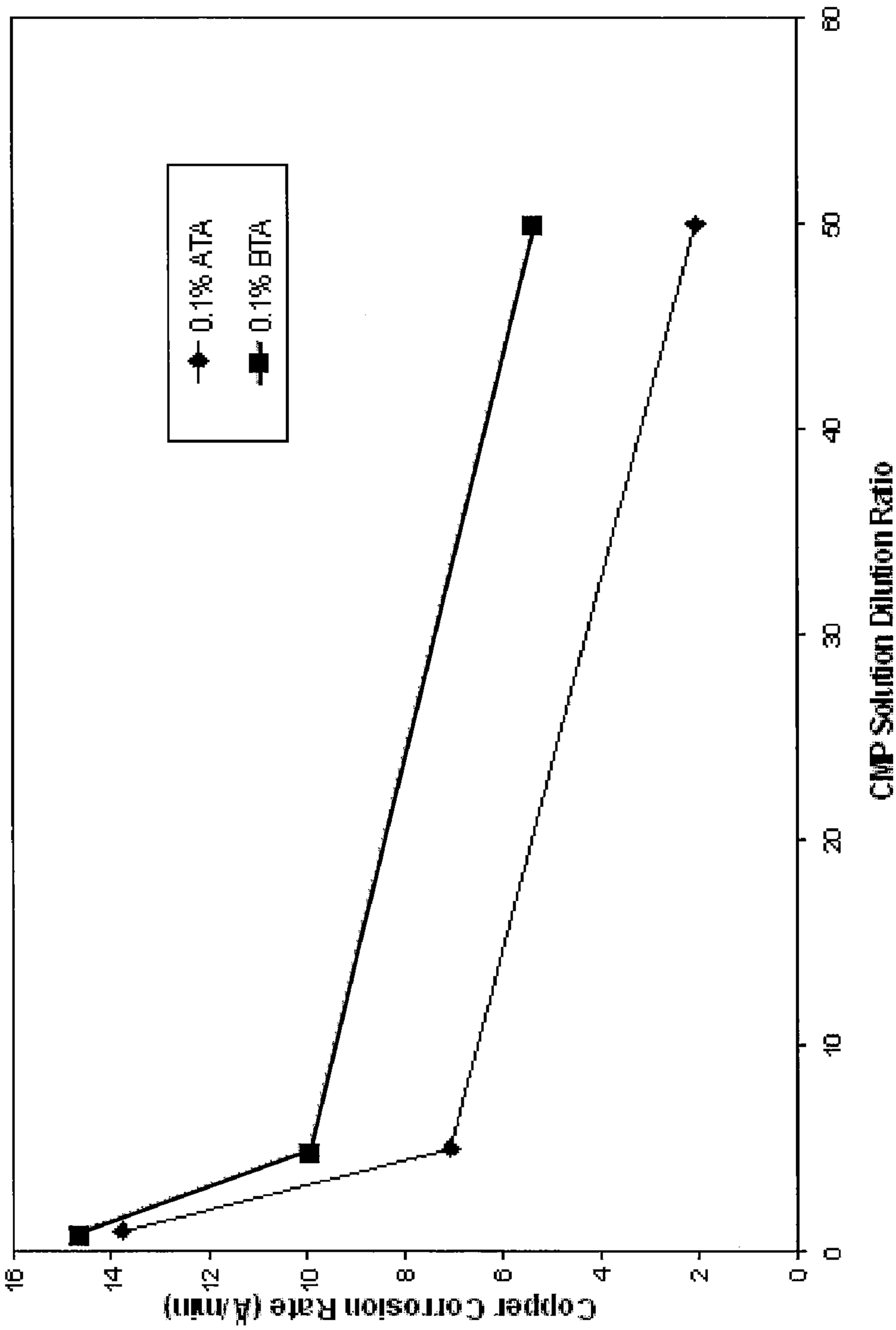

0.1% ATA
0.1% BTA
Copper Corrosion Rate (Å/min)
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
CMP Solution Dilution Ratio

FIGURE 1

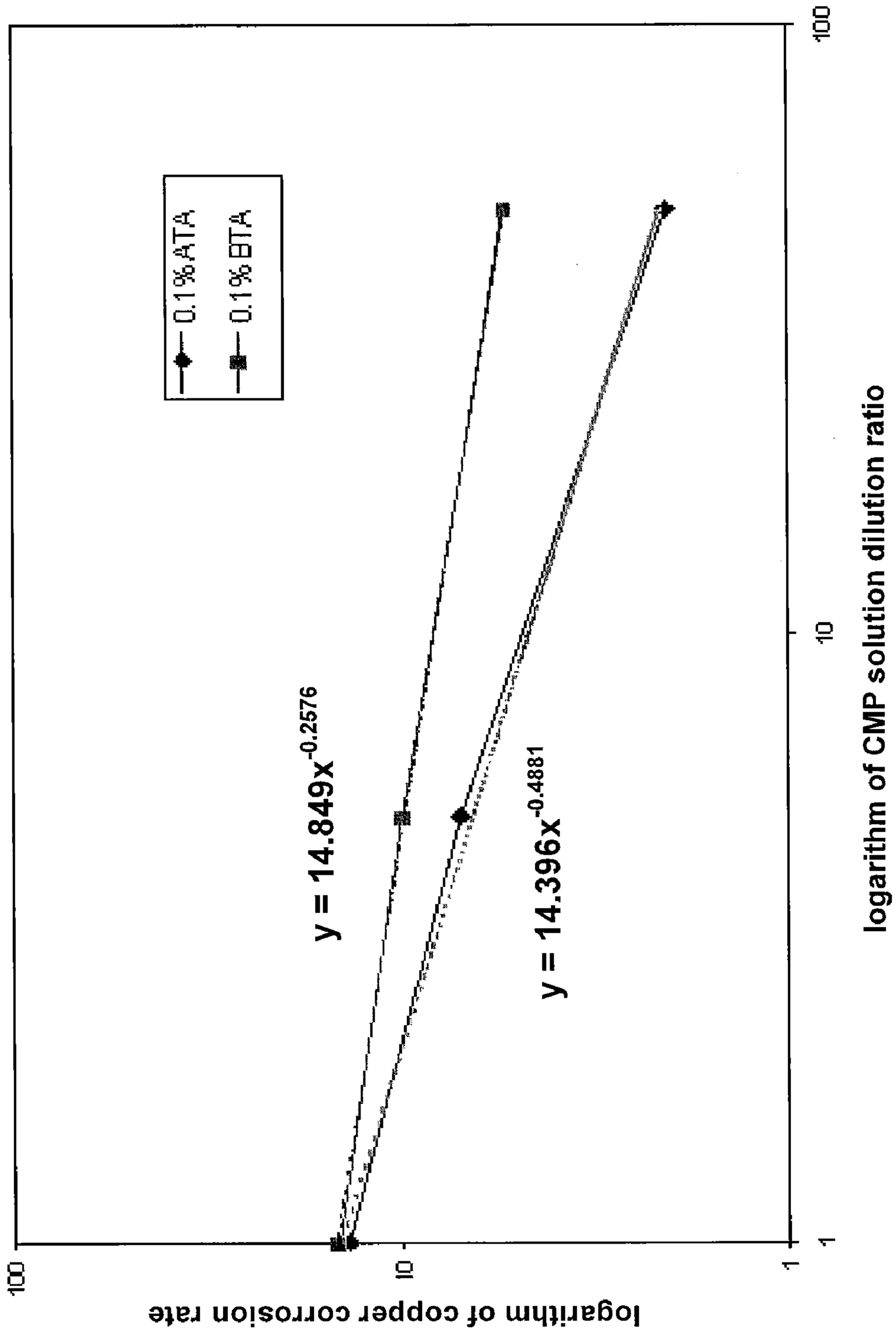

0.1% ATA
0.1% BTA
y = 14.849x^-0.2576
y = 14.396x^-0.4881
logarithm of copper corrosion rate
logarithm of CMP solution dilution ratio
100
10
1
1
10
100

FIGURE 2

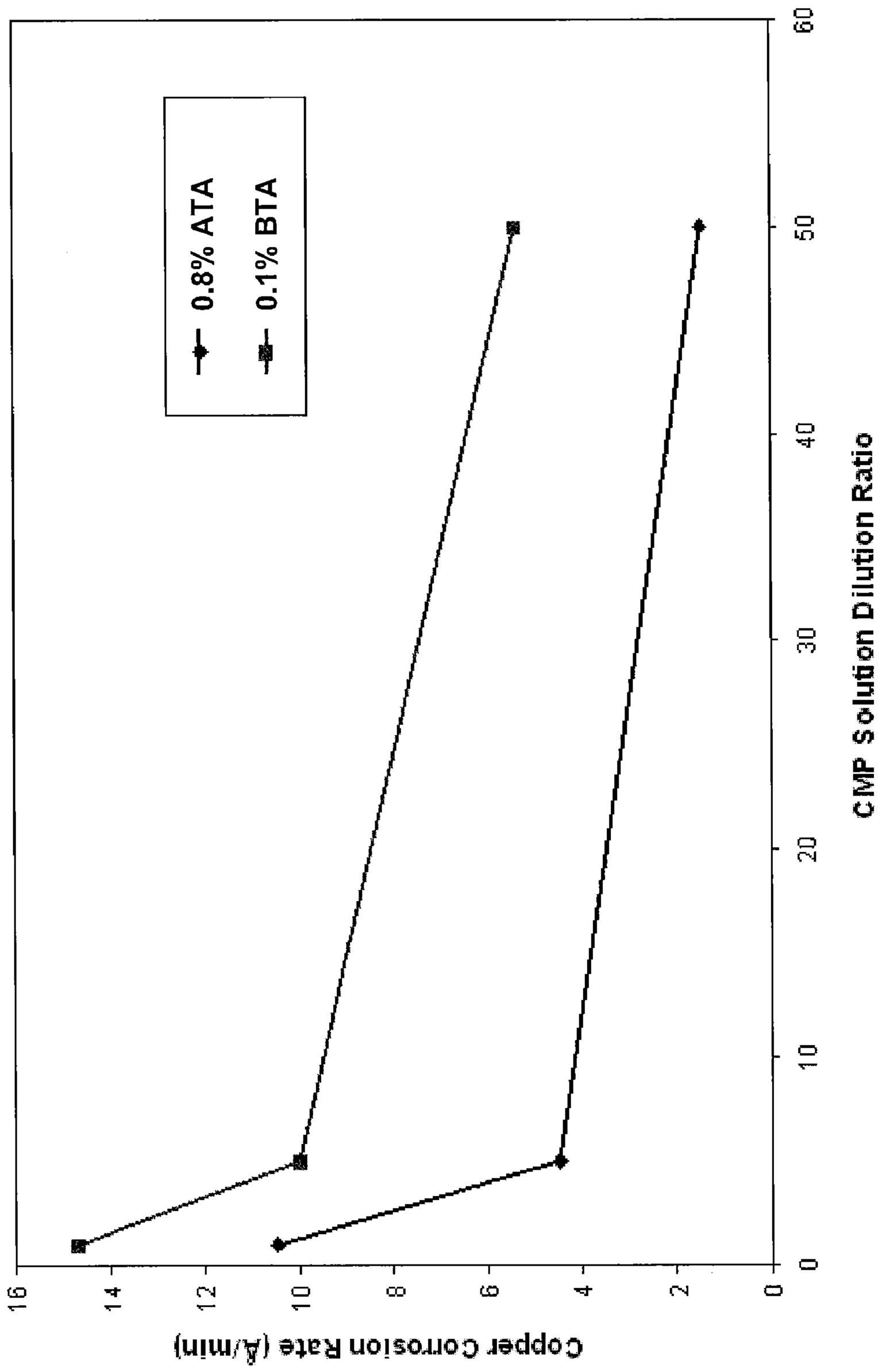

0.8% ATA
0.1% BTA
Copper Corrosion Rate (Å/min)
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
CMP Solution Dilution Ratio

FIGURE 3

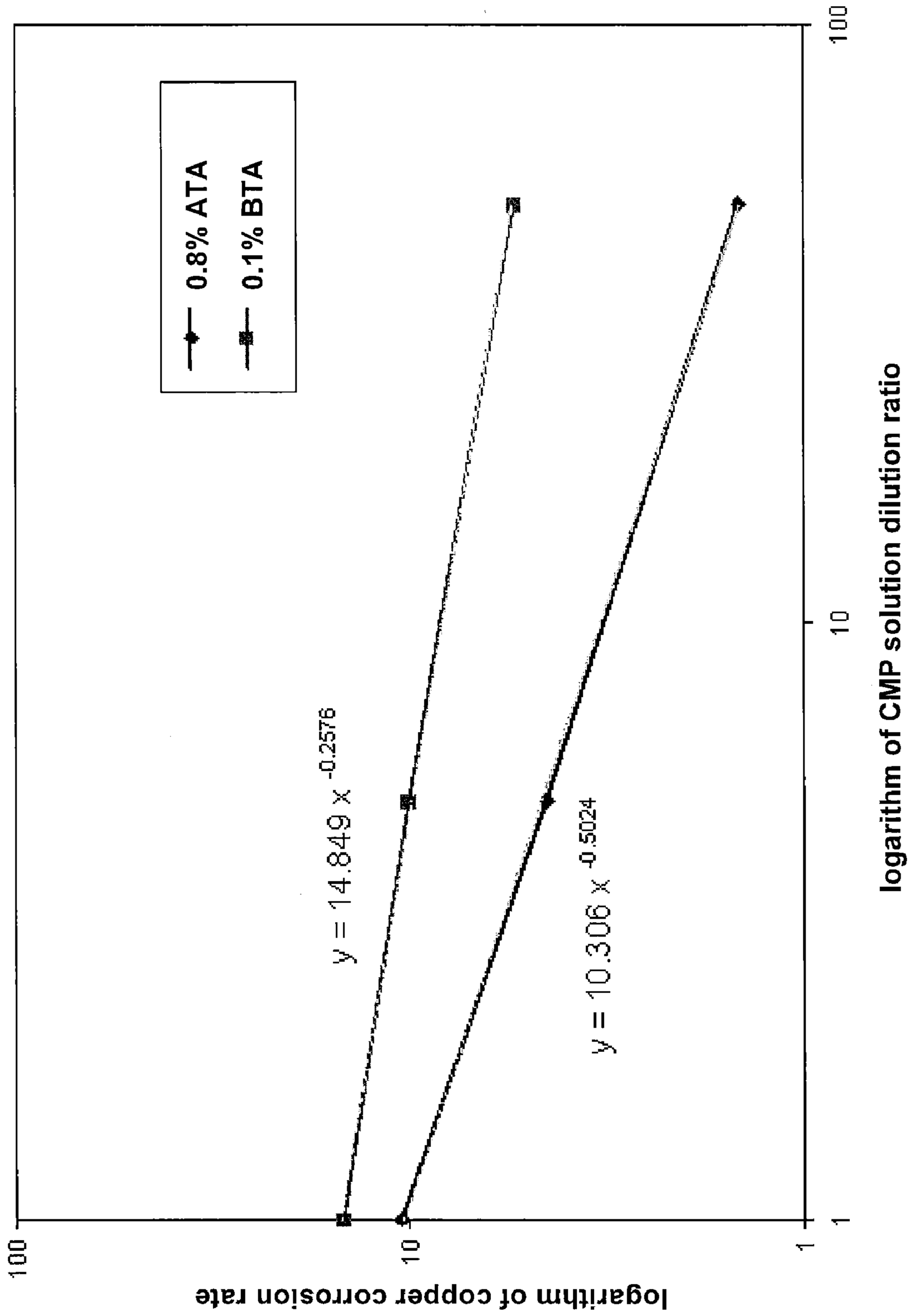

0.8% ATA
0.1% BTA
y = 14.849 x -0.2576
y = 10.306 x -0.5024
100
10
1
1
10
100
logarithm of copper corrosion rate
logarithm of CMP solution dilution ratio

FIGURE 4

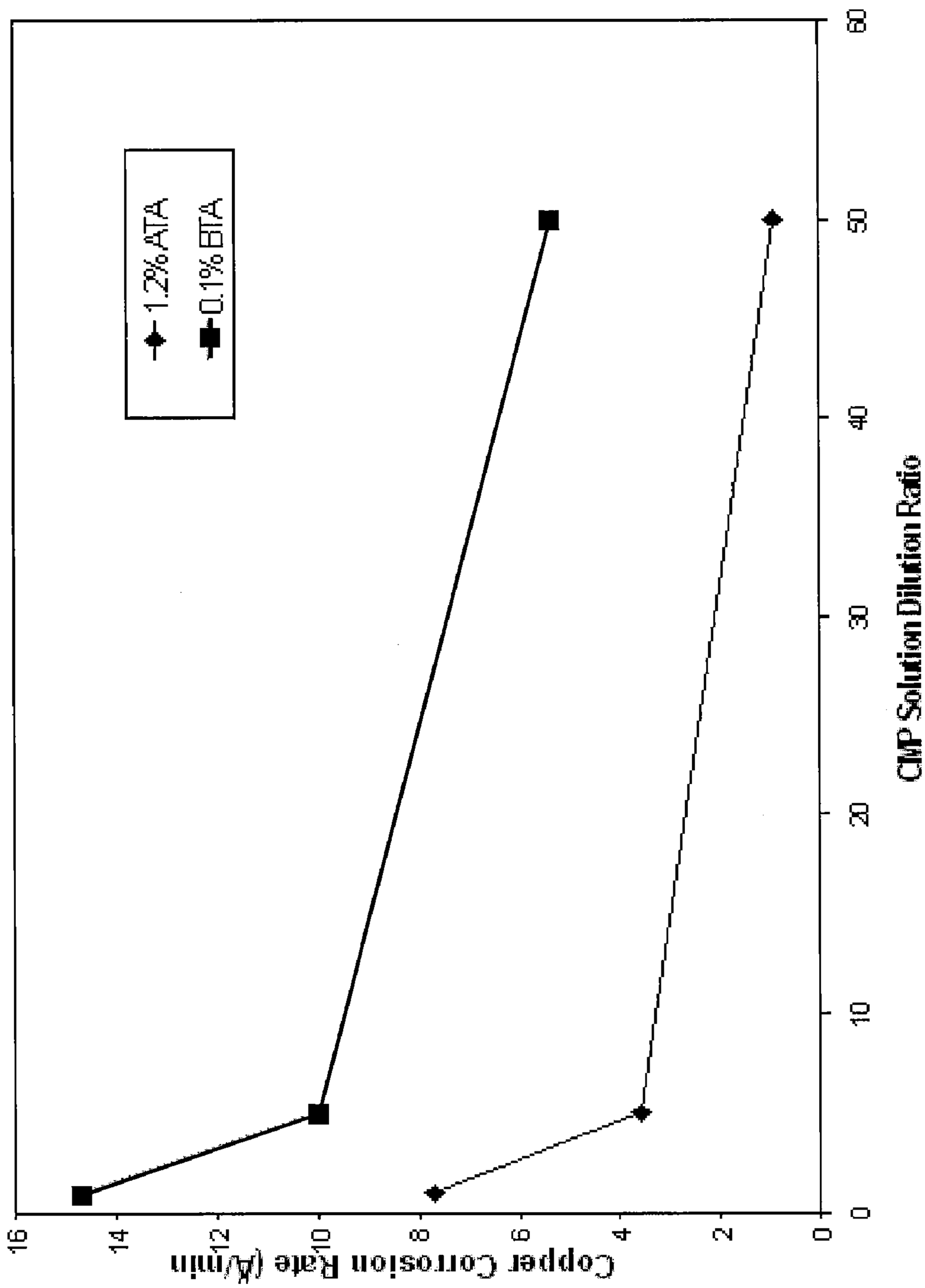

1.2% ATA
0.1% BTA
Copper Corrosion Rate (Å/min
CMP Solution Dilution Ratio
0
2
4
6
8
10
12
14
16
0
10
20
30
40
50
60

FIGURE 5

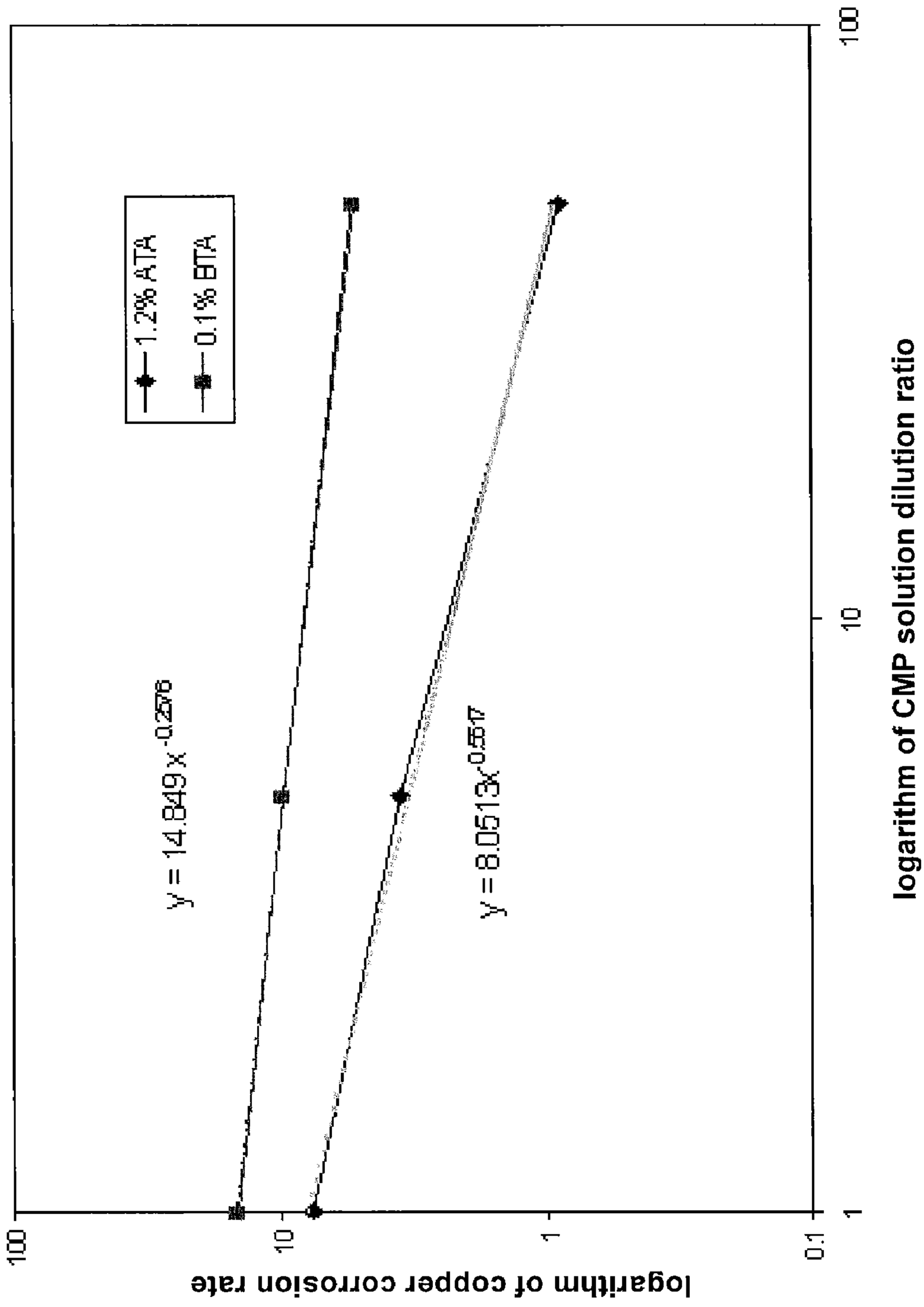

1.2% ATA
0.1% BTA
y = 14.849x^-0.2576
y = 8.0513x^-0.5517
100
10
1
0.1
1
10
100
logarithm of copper corrosion rate
logarithm of CMP solution dilution ratio

FIGURE 6

METHOD OF PASSIVATING CHEMICAL MECHANICAL POLISHING COMPOSITIONS FOR COPPER FILM PLANARIZATION PROCESSES

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 11/117,282 for "Method of Passivating Chemical Mechanical Polishing Compositions for Copper Film Planarization Processes," filed on Apr. 28, 2005 in the name of Jun Liu et al., now abandoned, which is a continuation-in-part of U.S. patent application Ser. No. 10/315,641 for "Passivative Chemical Mechanical Polishing Composition for Copper Film Planarization," filed on Dec. 10, 2002 in the name of Jun Liu et al., now U.S. Pat. No. 7,300,601, which are incorporated by reference herein in their entireties.

FIELD OF THE INVENTION

The present invention relates to a chemical mechanical polishing composition and to a method of using same for the polishing of wafer substrates having copper thereon, e.g., copper interconnects, electrodes, or metallization, as part of a microelectronic device structure.

DESCRIPTION OF THE RELATED ART

Copper is widely employed in semiconductor manufacturing as a material of construction for components of microelectronic device structures (e.g., contacts, electrodes, conductive vias, field emitter base layers, etc.), and it is rapidly becoming the interconnect metal of choice in semiconductor manufacturing due to its higher conductivity and increased electromigration resistance relative to aluminum and aluminum alloys.

Typically, the process scheme for utilizing copper in semiconductor manufacturing involves the damascene approach, wherein features are etched in a dielectric material. In the dual damascene process a single step is used to form both plugs and lines. Since copper has a propensity to diffuse into the dielectric material, leading to leakage between metal lines, barrier layers, such as Ta or TaN deposited by various deposition methods, are often used to seal the copper interconnects. Following deposition of the barrier layer material, a thin seed layer of copper is deposited on the barrier material via physical vapor deposition, followed by electrodeposition of copper to fill the features. The deposited copper must then be planarized to render it of suitable form to accommodate subsequent process steps in the fabrication of the finished semiconductor product, and in order to satisfactorily operate in the microcircuitry in which it is present. The planarization typically involves chemical mechanical polishing (CMP), using a CMP composition formulated for such purpose.

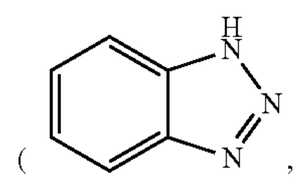
Due to the difference in chemical reactivity between copper and the barrier layer material, e.g. Ta and/or TaN, two chemically distinct slurries are often used in the copper CMP process. The Step I slurry is used to rapidly planarize the topography and remove the copper, with the Step I polish stopping at the barrier layer material. The Step II slurry removes the barrier layer material at a high removal rate and stops at the dielectric layer, or alternatively at a cap layer that has been applied to protect the dielectric.

Step I chemical mechanical polishing (CMP) compositions for planarization and polishing of copper typically are in the form of slurries containing an abrasive of suitable type,

e.g., an abrasive selected from among silica, alumina, and other oxides and mineralic materials, in a solvent medium containing one or more solvent species, e.g., water, organic solvents, etc. Typically, Step I slurries have a high copper removal rate, and a copper to barrier material removal rate selectivity of greater than 100:1.

One type of CMP composition for planarizing copper surfaces includes an aqueous slurry of abrasive particles containing hydrogen peroxide as an oxidizing component and glycine as a chelating agent. Glycine has been found to react with solution phase Cu^{+2} ions formed by the oxidation of the Cu metal to form a Cu^{2+}-glycine complex. The complexing of Cu^{+2} ions through formation of a water soluble Cu^{2+}-glycine chelate assists in removal of Cu in protruded regions via a direct dissolution mechanism, and the Cu^{2+}-glycine complex decomposes hydrogen peroxide to yield hydroxyl radicals which have a higher oxidation potential than hydrogen peroxide itself.

In step I CMP slurries, the compound benzotriazole (BTA) is often included as a corrosion inhibitor. In theory, BTA



(, FW: 119.13)

complexes with copper to form an insoluble Cu-BTA complex on the copper surface. The resulting insoluble protective film is meant to facilitate the planarization of the topography of the device structure being fabricated, since the recessed areas on the wafer surface are protected from dissolution, while mechanical action of the abrasive species on the protruding areas enables material removal and planarization to be carried out. Additionally, the Cu-BTA complex minimizes corrosion and preserves the functional integrity of the copper device structures for their intended use.

It is known that BTA functions well as a copper corrosion inhibitor in the absence of OH radicals. However, in step I copper CMP slurries containing hydrogen peroxide and glycine, the formation of highly oxidizing OH radicals under dynamic CMP conditions cannot be avoided, since copper metal is readily oxidized in such slurry environment. Experiments involving the addition of Cu^{2+} to an H_2O_2/glycine/BTA system have shown that the presence of Cu^{2+} increases the static etch rate of Cu dramatically, and at the same time, the Cu corrosion potential is shifted to less noble ranges.

The significance of this finding is that in the presence of H_2O_2 and glycine, BTA is not effective in protecting the low features of copper wafer surfaces during the CMP process, and thus undesired "dishing" and erosion occurs in high-density patterned areas on the wafer substrate.

Dishing occurs when too much copper is removed such that the copper surface is recessed relative to the barrier and/or dielectric surface of the semiconductor wafer. Dishing occurs when the copper and barrier material removal rates are disparate. Oxide erosion occurs when too much dielectric material is removed.

An alternative to the use of BTA as a corrosion inhibitor in CMP compositions includes 5-aminotetrazole (ATA), which is compatible with H_2O_2/glycine-based CMP compositions and effective to passivate copper surfaces when significant amounts of Cu ions are present in bulk solution and/or near the metal/solution interface during CMP processing.

During Step I, bulk copper is rapidly removed followed by the "soft landing" or "touchdown," whereby the polishing

conditions are altered until the underlying barrier material is exposed, as determinable using an endpoint detection system such as an in situ rate monitor (ISRM). Although the endpoint has been detected, signaling the exposure of the barrier layer material, copper overburden remains which must be removed and as such, an over-polishing step is often performed. Unfortunately, the "soft landing" and the over-polishing steps often result in dishing and/or erosion into copper features and thus, loss of wafer surface planarity and uniformity.

Step I CMP slurries advantageously remove copper rapidly during the step I CMP process. However, during the soft landing and/or over-polish, this rapid rate of copper removal may become disadvantageous as various surface defects such as recesses, erosion, dishing, etc., form on the copper layer surface. The net result of the overly aggressive step I slurry during soft landing and/or over-polish is a wafer substrate having a non-uniform planar surface, which can render the wafer unusable.

It would therefore be a significant advance in the art to provide a method that overcomes the deficiencies of the prior art relating to the rapid rate of copper removal during the soft landing and/or overpolishing steps of the step I CMP process. Specifically, it would be an advance in the art to provide a method to reduce the static etch rate of copper, and hence copper corrosion, during the soft landing and/or overpolishing steps of the step I polishing process.

SUMMARY OF THE INVENTION

The present invention relates to a chemical mechanical polishing composition and method of using same for the polishing of microelectronic device substrates having copper thereon. In addition, the present invention further relates to a method for slowing down the rate of copper removal during the soft landing and/or overpolishing steps of the step I polishing process.

In one aspect, the present invention relates to a method of determining a relationship between static etch rate and chemical mechanical polishing (CMP) composition dilution, said method comprising:

(a) preparing a first CMP composition;

(b) measuring a first static etch rate of a material to be polished using the first CMP composition;

(c) diluting the first CMP composition with a solvent to produce a second CMP composition;

(d) measuring a second static etch rate of the material to be polished using the second CMP composition;

(e) repeating steps (c) and (d) to produce a third CMP composition and measuring a third static etch rate;

(f) plotting static etch rate as a function of CMP composition dilution ratio using a logarithmic scale; and

(g) calculating the non-linear regression equation, wherein said regression equation is the relationship between static etch rate and CMP composition dilution.

In yet another aspect, the present invention relates to a kit comprising, in one or more containers, chemical mechanical polishing (CMP) composition reagents, wherein the CMP composition comprises 5-aminotetrazole (ATA), at least one oxidizing agent, at least one chelating agent and solvent, and wherein the kit is adapted to form a CMP composition suitable to planarize bulk copper and remove copper overburden from a microelectronic device having said copper thereon.

Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a plot of copper corrosion rate, in Angstroms per minute, as a function of 0.1% ATA/H_2O_2/glycine slurry dilution ratio (♦) and 0.1% BTA/H_2O_2/glycine slurry dilution ratio (■).

FIG. **2** is a logarithmic plot of the copper corrosion rate as a function of the ATA/H_2O_2/glycine slurry dilution ratio and the BTA/H_2O_2/glycine slurry dilution ratio illustrated in FIG. **1**.

FIG. **3** is a plot of copper corrosion rate, in Angstroms per minute, as a function of 0.8% ATA/H_2O_2/glycine slurry dilution ratio (♦) and 0.1% BTA/H_2O_2/glycine slurry dilution ratio (■).

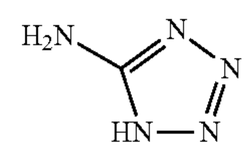
FIG. **4** is a logarithmic plot of the copper corrosion rate as a function of the ATA/H_2O_2/glycine slurry dilution ratio and the BTA/H_2O_2/glycine slurry dilution ratio illustrated in FIG. **3**.

FIG. **5** is a plot of copper corrosion rate, in Angstroms per minute, as a function of 1.2% ATA/H_2O_2/glycine slurry dilution ratio (♦) and 0.1% BTA/H_2O_2/glycine slurry dilution ratio (■).

FIG. **6** is a logarithmic plot of the copper corrosion rate as a function of the ATA/H_2O_2/glycine slurry dilution ratio and the BTA/H_2O_2/glycine slurry dilution ratio illustrated in FIG. **5**.

DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

The present invention is based on the discovery that 5-aminotetrazole (ATA,



(ATA, , FW: 85.06)

is unexpectedly effective as a replacement for BTA as a copper corrosion inhibitor in Step I CMP compositions for planarizing copper films. ATA is compatible with CMP compositions containing hydrogen peroxide as an oxidizer and glycine as a chelator. The ATA-containing CMP composition achieves active passivation of copper surfaces even when significant amounts of copper ions, e.g., Cu^{2+} cations, are present in bulk solution and/or at the metal/solution interface during CMP processing.

The present invention is further based on the discovery that dilution of a CMP slurry composition during the soft landing and/or over polishing step of a CMP process achies active passivation of exposed copper.

"Soft landing" or "touchdown," as defined herein, corresponds to some point in the Step I polishing process whereby the downforce pressure of the polisher may be decreased and/or the Step I composition altered to reduce dishing and/or erosion of the copper lines and plugs. Preferably, soft landing may be effectuated when the thickness of the layer of copper over the barrier material has been decreased to a range of from about 0.05 μm to about 0.4 μm.

"Over-polishing" is performed subsequent to soft landing to remove the copper overburden from the surface of the barrier material, while minimizing additional dishing or erosion of the copper features.

As used herein, "about" is intended to correspond to ±5% of the stated value.

"Microelectronic device," as used herein, corresponds to semiconductor substrates, flat panel displays, and microelectromechanical systems (MEMS). It is to be understood that the term "microelectronic device" is not meant to be limiting in any way and includes any substrate that will eventually become a microelectronic device.

As used herein, "suitability" to planarize bulk copper and remove copper overburden from a microelectronic device having said copper thereon corresponds to at least partial removal of said copper from the microelectronic device. Preferably, at least 90% of the copper is removed from the microelectronic device using the compositions of the invention, more preferably, at least 99% of the copper is removed.

As used herein, dilution of the CMP composition "subsequent" to the planarization of bulk copper corresponds to the soft landing step or immediately before the soft landing step.

The ATA-containing CMP compositions of the invention, in its broad contemplation, may be formulated with any suitable constituents, including any appropriate oxidizing agent(s), chelating agent(s), and corrosion inhibitor(s), abrasive media, solvent media, and optionally any suitable additives, adjuvants, excipients, etc., such as stabilizing agents, acids, bases (e.g., amines), surfactants, buffering agents, etc.

Oxidizing agents employed in the broad practice of the invention may be of any suitable type, including for example ferric nitrate, ferric ammonium oxalate, ferric ammonium citrate, permanganate salts (e.g., potassium permanganate), peroxyacids (e.g. peracetic acid), peroxoborate salts (e.g., potassium peroxoborate), urea-hydrogen peroxide, iodate salts (e.g., potassium iodate), perchlorate salts (e.g. tetramethylammonium perchlorate), persulfate salts, bromate salts, benzoquinone, chlorate salts, chlorite salts, hypochlorite salts, hypoiodite salts, oxybromide salts, percarbonate salts, periodate salts, ceric salts (e.g., ammonium ceric sulfate), chromate and dichromate compounds, cupricyanide and ferricyanide salts, ferriphenanthroline, ferripyridine and ferrocinium. Preferred oxidizers include peracetic acid, urea-hydrogen peroxide, di-t-butyl peroxide, benzyl peroxide, hydrogen peroxide and compatible mixtures including two or more of such oxidizer species.

Chelating agents in the CMP compositions of the invention may be of any appropriate type, including, for example: amino acids such as glycine, serine, proline, leucine, alanine, asparagine, aspartic acid, glutamine, valine, lysine, etc.; polyamine complexes and their salts, including ethylenediaminetetraacetic acid, N-hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic acid, iminodiacetic acid, diethylenetriaminepentaacetic acid, and ethanoldiglycinate; polycarboxylic acids, including phthalic acid, oxalic acid, malic acid, succinic acid, mandelic acid, and mellitic acid; and compatible mixtures including two or more of the foregoing species. Preferred chelating agents include amino acids, with glycine being most preferred.

The corrosion inhibitor component in the CMP composition of the invention comprises ATA, and may additionally include other corrosion inhibitor components in combination with ATA, in specific embodiments of the invention. Such other corrosion inhibitor components may be of any suitable type, including for example, imidazole, benzotriazole, benzimidazole, amino, imino, carboxy, mercapto, nitro, alkyl, urea and thiourea compounds and derivatives, etc. Preferred inhibitors include tetrazoles and their derivatives, and the invention therefore contemplates the provision of ATA alone or in combination with other tetrazole (or other corrosion inhibitor) species, as the corrosion inhibitor in compositions according to the present invention.

ATA is employed in CMP compositions of the invention in any suitable concentration. Suitable concentrations of ATA in a specific formulation are readily empirically determinable within the skill of the art, based on the disclosure herein, to provide a CMP composition with suitable copper surface passivation characteristics even in CMP environments containing high levels of copper cations. In one preferred embodiment of the invention, the amount of ATA in the CMP composition is in a range of from about 0.001 to about 10% by weight, based on the total weight of the CMP composition, with an amount of ATA in a range of from about 0.01 to about 5% by weight being more preferred, and an amount of ATA in a range of from about 0.10 to about 1.5% by weight being most preferred, based on the same total weight basis, although greater or lesser percentages may be employed to advantage in specific applications within the broad scope of the present invention.

The abrasive may be of any suitable type, including, without limitation, metal oxides, silicon nitrides, carbides, etc. Specific examples include silica, alumina, silicon carbide, silicon nitride, iron oxide, ceria, zirconium oxide, tin oxide, titanium dioxide, and mixtures of two or more of such components in suitable form, such as grains, granules, particles, or other divided form. Alternatively, the abrasive may include composite particles formed of two or more materials, e.g., NYACOL® alumina-coated colloidal silica (Nyacol Nano Technologies, Inc., Ashland, Mass.). Alumina is a preferred inorganic abrasive and may be employed in the form of boehmite or transitional δ, θ or γ phase alumina. Organic polymer particles, e.g., including thermoset and/or thermoplastic resin(s), may be utilized as abrasives. Useful resins in the broad practice of the present invention include epoxies, urethanes, polyesters, polyamides, polycarbonates, polyolefins, polyvinylchloride, polystyrenes, polyolefins, and (meth) acrylics. Mixtures of two or more organic polymer particles may be used as the abrasive medium, as well as particles comprising both inorganic and organic components.

Bases may be optionally employed for pH adjustment in compositions of the invention. Illustrative bases include, by way of example, potassium hydroxide, ammonium hydroxide and tetramethylammoniumhydroxide (TMAH), tetraethylammonium hydroxide, trimethyl hydroxyethylammonium hydroxide, methyl tri (hydroxyethyl) ammonium hydroxide, tetra(hydroxyethyl)ammonium hydroxide, and benzyl trimethylammonium hydroxide.

Acids may also be optionally employed for pH adjustment in compositions of the invention. The acids used may be of any suitable type, including, by way of example, formic acid, acetic acid, propanoic acid, butanoic acid, pentanoic acid, isovaleric acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, lactic acid, hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, hydrofluoric acid, malic acid, fumaric acid, malonic acid, glutaric acid, glycolic acid, salicylic acid, 1,2,3-benzenetricarboxylic acid, tartaric acid, gluconic acid, citric acid, phthalic acid, pyrocatechoic acid, pyrogallol carboxylic acid, gallic acid, tannic acid, and mixtures including two or more acids of the foregoing or other types.

Amines when present may be of any suitable type, including, by way of example, hydroxylamine, monoethanolamine, diethanolamine, triethanolamine, diethyleneglycolamine, N-hydroxylethylpiperazine, N-methylethanolamine, N,N-dimethylethanolamine, N-ethylethanolamine, N,N-diethylethanolamine, propanolamine, N,N-dimethylpropanolamine, N-ethylpropanolamine, N,N-diethylpropanolamine,

4-(2-hydroxyethyl)morpholine, aminoethylpiperazine, and mixtures including two or more of the foregoing or other amine species.

Surfactants when optionally employed in compositions of the invention may be of any suitable type, including non-ionic, anionic, cationic, and amphoteric surfactants, and polyelectrolytes including, for example: salts of organic acids; alkane sulfates (e.g., sodium dodecyl sulfate); alkane sulfonates; substituted amine salts (e.g., cetylpyridium bromide); betaines; polyethylene oxide; polyvinyl alcohol; polyvinyl acetate; polyacrylic acid; polyvinyl pyrrolidone; polyethyleneimine; and esters of anhydrosorbitols, such as those commercially available under the trademarks Tween® and Span®, as well as mixtures including two or more of the foregoing or other surfactant species.

The pH of CMP compositions of the invention may be at any suitable value that is efficacious for the specific polishing operation employed. In one embodiment, the pH of the CMP composition may be in a range of from about 2 to about 11, more preferably in a range of from about 2 to about 7, and most preferably in a range of from about 3 to about 6.

The solvents employed in CMP compositions of the invention may be single component solvents or multicomponent solvents, depending on the specific application. In one embodiment of the invention, the solvent in the CMP composition is water. In another embodiment, the solvent comprises an organic solvent, e.g., methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, glycerin, etc. In yet another embodiment, the solvent comprises a water-organic solvent solution. A wide variety of solvent types and specific solvent media may be employed in the general practice of the invention to provide a solvating/suspending medium in which the abrasive is dispersed and in which the other components are incorporated to provide a composition of appropriate character, e.g., of slurry form, for application to the platen of the CMP unit to provide a desired level of polishing of the copper on the wafer substrate.

In one embodiment, the invention provides a Step I CMP composition useful for chemical mechanical polishing of substrates having copper thereon, e.g., copper interconnects, metallization, device structural elements, etc., in which the composition includes hydrogen peroxide, glycine, ATA, and solvent.

In another embodiment, the invention provides a Step I CMP composition useful for chemical mechanical polishing of substrates having copper thereon, e.g., copper interconnects, metallization, device structural elements, etc., in which the composition includes hydrogen peroxide, glycine, ATA, abrasive and solvent.

In another embodiment, the CMP composition of the invention is an aqueous abrasive composition, and includes an aqueous medium, abrasive, ATA, H_2O_2 and glycine, wherein ATA, H_2O_2 and glycine have the following composition by weight, based on the total weight of the composition:

ATA	0.001-10 wt. %
H_2O_2	0.1-30 wt. %
Glycine	0.1-25 wt. %
Water	35-99.8 wt. %.

In a further specific illustrative embodiment, the CMP composition comprises the following components by weight, based on the total weight of the composition:

ATA	0.001-10 wt. %
H_2O_2	0.1-30 wt. %
Glycine	0.1-25 wt. %.
Abrasive	0.1-30 wt. %
Water	5-99.7 wt. %

with the total wt. % of all components in the composition totaling to 100 wt. %.

The CMP compositions of the invention may be provided as a single package formulation or a multi-part formulation that is mixed at the point of use or in a storage tank upstream of the tool. The advantage of a multi-part formulation resides in its extended shelf life relative to single-package formulations. A single package formulation is more susceptible to decomposition and change of its properties over time, in relation to a multi-part formulation, due to the presence of the oxidizer in the single-package CMP composition. The concentrations of the single-package formulation or the individual packages of the multi-part formulations may be widely varied in specific multiples, i.e., more dilute or more concentrated, in the broad practice of the invention, and it will be appreciated that the CMP compositions of the invention can variously and alternatively comprise, consist or consist essentially of any combination of ingredients consistent with the disclosure herein.

In one embodiment, each single ingredient of the CMP composition is individually delivered to the polishing table for combination at the table, to constitute the CMP composition for use. In another embodiment, the CMP composition is formulated as a two-part composition in which the first part comprises abrasive and corrosion inhibitor in aqueous medium, and the second part comprises oxidizing agent and chelating agent. In still another embodiment, the CMP composition is formulated as a two-part composition in which the first part comprises abrasive, corrosion inhibitor and chelating agent in an aqueous medium, and the second part comprises the oxidizer. In all of these various embodiments, the mixing of ingredients or parts to form the final composition occurs at the point of use, with mixing at the polishing table, polishing belt or the like, in an appropriate container shortly before reaching the polishing table, or at the CMP composition manufacturer and/or supplier.

Accordingly, another aspect of the invention relates to a kit including, in one or more containers, the components adapted to form the compositions of the invention as described hereinabove.

The copper CMP composition of the invention may be utilized in a conventional manner in the CMP operation, by application of the CMP composition to the copper surface on the microelectronic device substrate in a conventional fashion, and polishing of the copper surface may be carried out using a conventional polishing element such as a polishing pad, polishing belt, or the like.

The CMP composition of the invention is advantageously employed to polish surfaces of copper elements on microelectronic device substrates, without the occurrence of dishing or other adverse planarization deficiencies in the polished copper, even when significant amounts of copper ions, e.g., Cu^2, ions, are present in the bulk CMP slurry composition and/or at the copper/CMP slurry interface during CMP processing.

Step I CMP slurries advantageously remove copper rapidly during the step I CMP process. However, as the step I process enters the soft landing and/or overpolishing phases, this rapid rate of copper removal may become disadvantageous as vari-

ous surface defects such as recesses, erosion, dishing, etc., form on the copper layer surface.

To limit the overly aggressive CMP slurry composition during the soft landing and/or overpolishing steps of the Step I polishing step, the Step I CMP slurry of the invention may be diluted in a serial fashion. Accordingly, another embodiment of the present invention relates to a process of using a CMP composition to efficiently and uniformly planarize copper-containing microelectronic device substrates. Following rapid removal of the bulk copper layer using a more concentrated CMP composition, the CMP composition is diluted, either by in-line mixing or directly at the platen, to form a diluted CMP composition(s) for the soft landing and over-polishing steps. The diluting media most preferably corresponds to the solvent of the Step I CMP composition of the invention.

To demonstrate the effect of dilution on copper corrosion rates, Step I CMP compositions were diluted twice in a step-wise fashion and the Cu corrosion rates determined using electrochemical methods. As defined herein, "Cu corrosion rate" is equivalent to "static etch rate." By way of example, the initial Step I CMP compositions included 5 wt. % H_2O_2, 6 wt. % glycine, 1 wt. % abrasive, varying concentrations of ATA, and the balance water. To simulate the acceleration effect of corrosive copper ions in the solution, i.e., the formation of the Cu^{2+}-glycine complex which decomposes H_2O_2 to form the highly oxidizing OH radicals, 0.5 wt. % $CuSO_4.5H_2O$ was added to the initial Step I CMP compositions. In each case, the Step I CMP composition including ATA was compared to a Step I CMP composition including 5 wt. % H_2O_2, 6 wt. % glycine, 1 wt. % abrasive, 0.1 wt. % BTA, and the balance water

The initial Step I CMP composition (hereinafter Slurry1) was diluted step-wise with water to yield a second CMP slurry (1 part Slurry1 to 5 parts water; hereinafter Slurry2), and a third CMP slurry (1 part Slurry1 to 50 parts water; hereinafter Slurry3). The Cu corrosion rates in Angstroms per minute, were measured and the average Cu corrosion rate plotted as a function of CMP slurry dilution using both a linear and logarithmic scale.

Importantly, the number of serial dilutions of Slurry1, i.e., the most concentrated CMP slurry, is not limited to the aforementioned two dilutions. The number of dilutions depend on the desired end result of the Step I CMP polish and may vary from one step-wise dilution to ten step-wise dilutions. Alternatively, the dilution may be effectuated in a continuous manner whereby diluting solvent is continuously added to the CMP slurry during the soft-landing and/or over-polishing steps. In yet another alternative, Slurry1 is not diluted per se, but rather diluted CMP compositions are prepared for delivery of clean, diluted chemistries to the tool subsequent to the polish using Slurry1.

FIGS. **1** and **2** correspond to linear and logarithmic plots of the average Cu corrosion rate as a function of CMP slurry dilution for a Step I CMP slurry having an ATA concentration of 0.1 wt. %, respectively. Non-linear regression of the best-fit straight line in FIG. **2** yields a power relation between corrosion rate and slurry dilution of $y=14.396x^{-0.4881}$.

FIGS. **3** and **4** correspond to linear and logarithmic plots of the average Cu corrosion rate as a function of CMP slurry dilution for a Step I CMP slurry having an ATA concentration of 0.8 wt. %, respectively. Non-linear regression of the best-fit straight line in FIG. **4** yields a power relation between corrosion rate and slurry dilution of $y=10.306x^{-0.5024}$.

FIGS. **5** and **6** correspond to linear and logarithmic plots of the average Cu corrosion rate as a function of CMP slurry dilution for a Step I CMP slurry having an ATA concentration of 1.2 wt. %, respectively. Non-linear regression of the best-fit straight line in FIG. **6** yields a power relation between corrosion rate and slurry dilution of $y=8.0513x^{-0.5517}$.

In each example, the copper corrosion rate decreases with increasing slurry dilution. This may prove advantageous during the soft-landing and over-polishing steps to slow the copper corrosion rate and concomitantly minimize the dishing and erosion of the copper lines and plugs. Further, compared to compositions including BTA, ATA leads to a lower overall corrosion rate as well as a more rapid corrosion decrease with increasing dilution, as evidenced by the slopes of the regression lines.

These power relationships between copper corrosion rate and slurry dilution provide a means to control the static etch of Cu during Step I CMP polishing. In order to achieve acceptable planarization of the wafer surface at an efficient etch rate with the minimum amount of dishing, Slurry1 may be diluted at some point prior to the soft-landing, during the soft-landing and/or during the over-polishing steps of the Step I CMP polish, as readily determined by one skilled in the art. As defined herein, "bulk layer" represents the copper layer that is rapidly removed by the Step I CMP composition of the invention, e.g., Slurry1, and "residual layer" represents the copper layer that remains following the removal of the bulk layer, including the copper overburden, which is intended to be removed at a slower rate, e.g., by Slurry2, Slurry3, etc. By diluting the overly aggressive Slurry1 at the appropriate point in the CMP polish, polishing defects such as dishing and erosion are substantially eliminated.

The diluting solvent, e.g., water, may be delivered to the polishing table at the appropriate time and in the appropriate amount based on the regression equation specific to the slurry composition of choice, as readily determinable by one skilled in the art. In practice, Slurry1 may be diluted in a serial manner and the Cu corrosion rate of each composition measured using Tafel or some equivalent measurement. Thereafter, a logarithmic plot of the Cu corrosion rate as a function of the slurry dilution may be plotted and the non-linear regression equation calculated. Using the regression equation and knowledge of the wafer to be polished, e.g., thickness of the film, removal rate, etc., one skilled in the art may determine the appropriate time and in the appropriate amount of diluting solvent to deliver to the polishing table to slow the static etch rate of copper to a rate that minimizes the formation of polishing defects such as dishing.

The CMP composition of the invention may be diluted in a serial manner to effectuate substantial removal of the residual layer of copper while simultaneously minimizing dishing and erosion of the copper lines and plugs, as readily determined by one skilled in the art. As defined herein, "substantial removal" corresponds to at least 80%, preferably at least 90%, most preferably at least 95% of the residual layer of copper is removed using the series of Step I CMP compositions.

It is also contemplated herein that the dilution process may be automated whereby the polishing table and a programmable logic control (PLC) unit may be communicatively connected and the regression equation for the CMP slurry of choice input into the PLC. At the appropriate time, the appropriate amount of diluting solvent will be delivered to the polishing table, as controlled by the PLC.

Following completion of the Step I CMP process, the platen and substrate are rinsed with solvent. Preferably, the solvent is the same as that used in the Step I CMP compositions described herein, e.g., water. The rinse time may be in a range from about 5 sec to about 30 sec, preferably about 10

sec to about 20 sec. Thereafter, the wafer substrate may be transferred to another platen for Step II polishing thereon.

While the invention has been described herein in reference to specific aspects, features and illustrative embodiments of the invention, it will be appreciated that the utility of the invention is not thus limited, but rather extends to and encompasses numerous other variations, modifications and alternative embodiments, as will suggest themselves to those of ordinary skill in the field of the present invention, based on the disclosure herein. Correspondingly, the invention as hereinafter claimed is intended to be broadly construed and interpreted, as including all such variations, modifications and alternative embodiments, within its spirit and scope.

What is claimed is:

1. A method of fabricating a microelectronic device, said method comprising:

(a) preparing a multi-component chemical mechanical polishing (CMP) composition by combining at least two separate materials at a locus, wherein one of the at least two materials comprises abrasive and at least one corrosion inhibitor and the other of the at least two materials comprises at least one oxidizing agent;

(b) contacting metal on a substrate under CMP conditions effective to planarize metal with said CMP composition;

(c) diluting said CMP composition with solvent to produce a dilute CMP composition; and

(d) contacting the metal of step (b) with the dilute CMP composition under CMP conditions effective to remove metal overburden and expose a barrier material layer,

wherein said microelectronic device comprises a substrate.

2. The method of claim **1**, wherein one or more of the at least two materials further comprises at least one chelating agent.

3. The method of claim **1**, wherein the corrosion inhibitor comprises 5-aminotetrazole (ATA).

4. The method of claim **1**, wherein the metal comprises copper.

5. The method of claim **1**, wherein the at least two materials are combined at a locus selected from the group consisting of: at the point of use; at the polishing apparatus; and in a container upstream of the polishing apparatus.

6. The method of claim **1**, wherein the at least one oxidizing agent comprises a compound selected from the group consisting of ferric nitrate, ferric ammonium oxalate, ferric ammonium citrate, permanganate salts, peroxyacids, peroxoborate salts, urea-hydrogen peroxide, iodate salts, perchlorate salts, persulfate salts, bromate salts, benzoquinone, chlorate salts, chlorite salts, hypochlorite salts, hypoiodite salts, oxybromide salts, percarbonate salts, periodate salts, ceric salts, chromate and dichromate compounds, cupricyanide and ferricyanide salts, ferriphenanthroline, ferripyridine, ferrocinium, peracetic acid, di-t-butyl peroxide, benzyl peroxide, hydrogen peroxide, and compatible mixtures including two or more of such oxidizer species.

7. The method of claim **2**, wherein the at least one chelating agent comprises a compound selected from the group consisting of glycine, serine, proline, leucine, alanine, asparagine, aspartic acid, glutamine, valine, lysine, polyamine complexes and their salts, polycarboxylic acids, and compatible mixtures including two or more of the foregoing species.

8. The method of claim **1**, wherein the at least one abrasive comprises a material selected from the group consisting of silica, alumina, silicon carbide, silicon nitride, iron oxide, ceria, zirconium oxide, tin oxide, titanium dioxide, and mixtures of two or more of such components in suitable form.

9. The method of claim **1**, wherein the at least one abrasive comprises alumina-coated colloidal silica.

10. The method of claim **1**, wherein the solvent comprises a species selected from the group consisting of water, methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, glycerin, and combinations thereof

11. The method of claim **1**, wherein the solvent comprises water.

12. The method of claim **1**, wherein the barrier layer material comprises tantalum.

13. The method of claim **1**, wherein at least one of the materials further comprise an component selected from the group consisting of at least one base, at least one acid, at least one amine, at least one surfactant, at least one organic solvent, and combinations thereof.

14. The method of claim **1**, wherein the CMP composition is diluted with solvent in a dilution range from about 1:2 to about 1:100.

15. The method of claim **1**, wherein the CMP composition is diluted with solvent in a dilution range from about 1:5 to about 1:50.

16. The method of claim **1**, wherein a static etch rate of metal using the CMP composition is greater than the static etch rate of metal using the dilute CMP composition.

17. The method of claim **1**, further comprising diluting the dilute CMP composition with solvent to produce a second dilute CMP composition and contacting the metal of step (d) with the second dilute CMP composition under CMP conditions for a sufficient time and under sufficient contacting conditions to substantially remove the metal overburden and expose the barrier material layer.

18. The method of claim **1**, wherein dilution is effectuated in steps or continuously.

19. The method of claim **1**, wherein the CMP composition is diluted to produce the dilute CMP composition by in-line mixing or directly at a CMP platen.

20. The method of claim **1**, wherein the CMP composition is diluted to produce the dilute CMP composition at a process point selected from the group consisting of:

prior to soft-landing, during soft-landing, and during over-polishing.

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